THE IN-PLACE

POLLUTANTS PROGRAM

BACKGROUND AND

THEORETICAL CONCEPTS

- VOLUME II

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IN-PLACE POLLUTANTS PROGRAM - VOLUME II

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PREFACE

The In-Place Pollutants Program addresses the impact of contaminants in sediment on overlying water quality and aquatic biota with the aim of developing strategies for the management of contaminated sediments.

This report, Volume II, provides the background and an overview of the theoretical concepts related to the program and companion volumes will provide the following:

Volume I: In-Place Pollutants Program - A Program Overview.
            (expected March, 1987).

Volume III: Phase 1 Studies.
            (expected April, 1987).

Volume IV: Phase 1 Data Summary.
            (expected April, 1987)

Subsequent studies will be reported in other volumes in the series.

ACKNOWLEDGEMENTS

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CHAPTER I - INTRODUCTION

1.1 BACKGROUND

The study of in-place pollutants, defined as inorganic and organic contaminants in sediment, is designed to increase our knowledge of the influence of contaminants in bottom sediment on the aquatic ecosystem.

The concept of contaminated sediment as a potential source of pollutants grew out of findings from sediment studies associated mainly with dredging. During the early 1970's, the need to control contaminants in dredged sediments became apparent as a result of studies that identified the absence of certain benthic indicator species in harbours with contaminated sediments (Persaud and Wilkins, 1976). These early studies did not establish specific biological impacts of contaminants in sediments on aquatic biota but identified that certain elevated levels of contaminants were associated with the absence of certain benthic indicator species. The results from this early work were used in the development of a set of bulk chemical guidelines for evaluating dredged material for open-water disposal (Persaud and Wilkins, 1976). The guidelines are also used to evaluate sediment quality during routine surveillance and monitoring studies.

The bulk chemical guidelines, developed mainly for metals, nutrients, PCB's and oil and grease, address the 'total' amounts of the respective chemical present in a given sediment sample. This approach may be used for basic guidance in environmental protection but is not totally satisfactory for assessing the biological significance of contaminants in sediment, especially the heavy metals of which only a fraction of the total may be bioavailable or can be released to the water column. Appropriate procedures had to be developed to properly address the significance of contaminated sediments with respect to the organisms inhabiting the aquatic ecosystem.

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The main issues in this regard relate to:
- the potential release of contaminants in sediment to the overlying water
- the toxic (lethal and sublethal) effects on bottom-dwelling (benthic) organisms
- the uptake (bioaccumulation) of contaminants from sediments by benthic organisms.

1.2 THE ORIGIN AND SIGNIFICANCE OF IN-PLACE POLLUTANTS

Contaminants that enter the aquatic environment may exist as distinct entities, dissolved in water or attached to particulate matter depending on the physical and chemical properties of the contaminants. Much of the dissolved contaminants that are not volatilized to the atmosphere are taken up by aquatic plants and animals or precipitate out of solution and become incorporated in bottom sediments.

Most chlorinated hydrocarbons and metals have a strong affinity for particulate matter such as fine-grained sediment (silt/clay), organic detritus and algae. As a result, these contaminants adsorb onto particulates in the water column and eventually settle with the particulates to the bottom.

The particulates act as 'scavengers' or 'carrier particles' in removing contaminants from the water column and concentrating them in bottom sediments which become a 'sink' for a variety of contaminants. Because bottom sediment acts as a sink and changes very slowly, it makes a very good medium for monitoring historical trends and sources of pollution.

It was previously thought that, once contaminants enter the sediment, they are effectively 'locked-up' from the rest of the ecosystem. Evidence (Zepp, 1978), however, indicates that sorption of contaminants to sediment is a reversible process and contaminated sediments may be a continual source of contaminants to water and fish after external inputs (point and non-point sources of contaminants) have ceased. Field and laboratory studies (Eadie et al., 1982, Meier and Rediske, 1984)

suggest benthic organisms can take up and concentrate contaminants directly from sediments.

The significance of in-place pollutants has been identified in a report by the International Joint Commission (IJC, 1985) on Great Lakes Water Quality where it was pointed out that 38 of the 42 areas of concern around the Great Lakes have moderately to heavily contaminated sediments and these in-place pollutants are considered to be the most common sources of continuing water quality problems. (IJC, 1985). Although harbours, because of their generally poor hydrodynamic characteristics (lack of currents and barriers to water movement), present ideal situations for the accumulation of contaminants in sediments (in-place pollutants), other nearshore 'depositional' areas, such as embayments are also found to have highly contaminated sediments (Persaud et al., 1985).

1.3 THE IN-PLACE POLLUTANTS PROGRAM

The MOE In-Place Pollutants Program began in 1983 and was designed to initially provide the necessary basis, through field studies, to understand how contaminated sediments affect water quality, benthic macroinvertebrates and bottom feeding fish. With a basic understanding of in-place pollutants established, efforts are being directed towards defining the mechanisms of contaminant uptake by organisms, the sublethal effects of contaminants on organisms and factors affecting the movement and fate of contaminants in sediments. The information gatherered through such studies would provide guidance on improving bulk chemical guidelines to reflect the biological significance of contaminants in sediment and to establish guidelines for additional parameters of concern.

The Program initially focused on two major groups of chemicals; the heavy metals and the organochlorine compounds (PCB and selected pesticides). This narrow group of contaminants was selected because it is extremely difficult, under field conditions, to isolate the biological impacts of specific contaminants from the heterogeneous mass of chemical substances that may exist in sediment. Sediment

bioassessment procedures using laboratory microcosms are also being developed to provide the basis for examining the toxic or bioaccumulative aspects of specific chemicals or groups of chemicals on aquatic biota.

The Program design has also taken into account the uneven distribution of contaminants in sediment within and between geographical locations (Namminga and Wilhm 1977; Glooschenko et al, 1981; Persaud et al, 1985). The initial phase of the program involved data collection from various locations of the lower Great Lakes and the interconnecting channels. This provided indications of how different sediment types and degree of contamination may affect the indigenous benthic population. Current in-place pollutant investigations are carried on in an intensive fashion in fewer geographical areas.

The information obtained from the In-Place Pollutants Program will provide the scientific basis for developing strategies for the management of contaminated sediments. The objectives of this program are outlined below. A comprehensive overview of the Program is outlined in another report, Program Summary, Volume I.

1.3.1   Program Objectives

The objective of the In-Place Pollutants Program is:

to determine the potential impacts of contaminants in sediments on overlying water quality and on aquatic biota and to develop strategies for the management of contaminated sediments that will ensure the protection of water quality and water uses. This will involve the investigation of bottom water chemistry, sediment chemistry, fate and transport of sediments and associated contaminants, toxicity of contaminated sediments to biota and the bioaccumlation potential of contaminants in sediments.

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To achieve this objective, the following tasks are being undertaken:

1. Characterize sediment type and chemistry in areas of known sediment contamination in Ontario.

2. Determine the fate of contaminants in sediments by assessing the physical transport of sediments into and out of selected areas.

3. Evaluate the toxicity of contaminated sediments to aquatic biota that are representative of those found in Ontario's aquatic environment through the use of in-situ and laboratory testing.

4. Evaluate the bioaccumulation of contaminants from sediments in biota and determine the mechanism of transport of contaminants from sediments into biota.

5. Determine the mechanism of transport of contaminants from sediments into the water column and biota.

The remaining sections of this volume provide an overview of relevant background information on the sources and properties of metals and organic contaminants in the aquatic system and their influence on benthic organisms. Certain terms will be used in the text of this report and the definitions are as follows:

Bioaccumulation — Uptake and retention of environmental substances by aquatic organisms from both the environment (water, sediment) and food.

Bioconcentration Factor — The ratio of the measured residue in the biota compared to the residue of the substance in the ambient air, water or sediment environment of the organism.

Biomagnification   –   The magnification (increase in
                        concentration) of an environmental
                        substance through the food chain.

CHAPTER II - THEORETICAL CONCEPTS - AN OVERVIEW

2.1 SOURCES AND PROPERTIES OF METALS IN THE AQUATIC ENVIRONMENT

The metals of environmental concern are those normally referred to as
trace metals or heavy metals. These terms are often used interchange-
ably. Heavy metals can be defined as those metals with a density
greater than 5 gcm^{-3} (Hakanson and Jansson, 1983), or specific gravity
of over 4.5 (Jarvis, 1983). Trace metals are regarded as those found in
small concentrations in biological systems and may be essential to life
(Forstner and Wittman, 1981).

Organisms have a wide range of tolerance for some metals such as copper,
iron, manganese and zinc while exhibiting a narrow tolerance range for
others such as mercury and lead. For the purposes of this report the
metals of interest are the heavy metals with known toxic properties and
include cadmium (Cd), chromium (Cr), lead (Pb), copper (Cu), mercury
(Hg), nickel (Ni) and zinc (Zn). Iron (Fe) and manganese (Mn) have been
included because of their important influence on the fate of other
metals in the aquatic environment.

Arsenic which is a metalloid (exhibiting properties of both metals and
non-metals) has also been included among the heavy metals considered in
this study. Of the metals listed above, lead, cadmium, mercury and
arsenic are of major concern from an ecosystem 'health' perspective.

Heavy metals in sediments are derived primarily from natural sources
(termed lithogenic or geochemical sources) and man-made sources such as
industrial or mining processes (referred to as anthropogenic sources).
In most cases certain forms (those available to aquatic life) in which a
metal exists in the environment are of greater importance from a
toxicological point of view than the total concentrations of the metal.

2.1.1   Lithogenic Sources of Metals

The primary source of heavy metals is rock. Rock that is exposed
at or just below the earth's surface undergoes physical and
chemical weathering which transforms the rock into small mineral
fragments which make up the inorganic component of soil.

The breakdown of rock results in the release of many metals which
are of a size that can be easily transported by water. The heavy
metal concentration in a given soil will therefore be a reflection
of the chemical composition of the parent rock material from which
the soil was derived providing there are no major anthropogenic
additions.

When water and soils interact the soil minerals may undergo further
chemical transformations that release individual heavy metals which
can then be transported and deposited great distances from their
origin. Water and sediment in areas of metal-bearing bedrock will
also contain relatively high levels of those metals present in the
bedrock.

2.1.2   Anthropogenic Sources of Metals

The waste products of many metal processing and other chemical
industries using metallic compounds can contain significant
quantities of heavy metals which find their way into the aquatic
environment. Municipal wastes (storm and sanitary discharges)
resulting from urban runoff and domestic sewage discharges also
contain varying levels of metals. Atmospheric emissions
originating from natural sources (e.g. volcanoes) as well as
manmade sources (e.g. industries, automobile exhausts) also .
contribute to the overall loading of various metals to the aquatic
environment.

2.1.3 Fate of Metals in the Aquatic Environment

Heavy metals are introduced into the aquatic environment in solid, dissolved or colloidal forms*. The solids include various mineral forms and metals adsorbed onto particulates such as organic matter. The dissolved fraction (defined as that fraction which will pass through a 0.45 μm filter) includes the ionic forms of metals (cations) and metal complexes formed with dissolved organic matter. Metals in the dissolved fraction can be adsorbed onto particulate matter or be taken up by aquatic organisms.

The fate of heavy metals in the aquatic environment is to a great extent governed by the physicochemical conditions of the environment. The three important conditions are Eh, pH and availability of sorbing materials.

Eh or redox potential is a measure of the concentration of electrons in a medium (a positive Eh value is indicative of an oxidizing environment - presence of free or dissolved oxygen while a negative value suggests a reducing environment - absence of oxygen). pH is a measure of the hydrogen ion (H^+) concentration (acidity or alkalinity) in a given solution.

The sorbing agents of metals in the aquatic environment include minerals such as clays, organic detritus, algae and the hydrous oxides of iron and manganese. Metals may also be coprecipitated with hydrous iron, manganese oxides and iron sulphides. Metals that are adsorbed onto or coprecipitated with particulate matter eventually settle to the bottom of water courses and become incorporated in sediments.

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* Colloids range in size from 10^{-4} μm to 1 μm. A small volume can adsorb large quantities of metals because of the large surface area to volume ratio and an overall negative charge.

2.1.4   Mechanisms of Sediment - Metal Association

Metals derived from natural sources, such as the weathering of
bedrock, may to a large extent exist in the mineral forms of the
clay-sized sediment fraction. The term clay is used to denote the
physical size. For example, clay refers to particles smaller than
2 μm as opposed to clay minerals which are aluminosilicate minerals
occurring in the clay-sized fraction of sediments. The clays, by
virtue of the presence of these metallic clay minerals as well as
other fine-grained particulates (such as organic material) will
contain significantly higher levels of metals as opposed to
coarse-grained sediment such as sand which is made up mainly of
quartz and feldspars with very low heavy metal contents (Forstner
and Wittman, 1981).

Certain metals in fine-grained minerals often occupy positions in
the lattice structure of the minerals. The metals in these
positions are considered inert in that they are not biologically
available. The availability of metals in other types of
association with various sediment fractions depends on how tightly
the metals are bonded to the sediment and factors such as the Eh
and pH of the sediment. The various associations between metals
and the different materials making up sediment are referred to as
geochemical partitioning. Metals are associated with the sediments
by processes such as adsorption, co-precipitation and
complexation.

2.1.4.1   Adsorption of Metals

Naturally occurring colloidal material such as the hydrous
oxides of iron and manganese, organic matter and clays form
ideal substrates for metal adsorption. The surfaces of these
materials
are negatively charged and attract the positively charged
metal ions (cations) which become adsorbed onto the
particulates mainly through electrostatic forces. This type
of adsorption is referred to as non-specific adsorption where

the cations attach onto any available site (non-selective).
This type of metal-sediment association is referred to as the
easily exchangeable or cation exchange phase. There is a
continuous exchange of cations between the sorbing agents and
the surrounding water.

Some cations can adsorb strongly to particulate matter forming
specific chemical bonds. This type of adsorption is referred
to as specific adsorption and the cations are not as easily
released as in the exchangeable form.

2.1.4.2   Co-precipitation of Metals

The hydrous oxides of iron and manganese can form coatings on
mineral surfaces such as clays and as they precipitate, the
negative charge on the oxide can attract metals which become
incorporated in the lattice of the coating. This is referred
to as co-precipitation.

Co-precipitated metals may be residual (derived from natural
sources through weathering) or obtained from solution. The
ease with which co-precipitated metals are released depends on
the nature of the chemical bonding. Freshly precipitated
metals can be released with ease but over time the bond
strengthens and release becomes more difficult.

Hydrous oxides of iron and manganese are good scavengers of
metals under oxidizing conditions such as in the water column
but under reducing conditions (absence of oxygen) they may
become soluble thus releasing the metals that have bonded to
the surface.

Metals in this geochemical phase (hydrous oxides) are referred
to as "easily reducible" or "moderately reducible" depending
on the ease or difficulty with which they can be released.

2.1.4.3 Complexation of Metals

Metals can form bonds with many natural and synthetic organic compounds, a process known as complexation or metal-organic complex formation. Metals may form bonds of moderate strength by replacing the H^+ on the -COOH and -OH groups of organic acids. Strong bonds are created when metals attach directly to carbon atoms forming organo-metallic compounds. Strong bonds are also formed when metals attach to two or more sites of the organic molecule where the metal is said to be chelated.

Metal-organic complexes can precipitate directly or adsorb onto solids such as clay minerals.

2.1.5 The Influence of Eh and pH on Metal-Sediment Associations

Eh or the oxidation-reduction (redox) potential is a measure of the ability of a medium to accept or supply electrons during chemical (oxidation-reduction) reactions. Oxidation refers to a loss of electrons by a chemical 'agent' (electron donor) and reduction is a gain of electrons by another agent (receptor). For example, when hydrogen and oxygen combine to form water ($2H_2 + O_2 \longrightarrow 2H_2O$) the hydrogen is oxidized (loss of electrons) by the oxidizing agent (oxygen). In the process the oxygen is reduced (gain electrons). Oxygen is the strongest oxidizing agent found in nature.

Eh is usually measured in millivolts and positive values (between 0 and 1000) indicate oxidizing conditions which would for example, exist in an oxygenated water column. Negative values (between 0 and - 1000) are indicative of reducing conditions such as highly organic bottom sediments where the lack of oxygen creates anaerobic conditions.

The Eh of a medium greatly influences chemical reactions involving iron and manganese oxides which have a great bearing on the fate of

heavy metals in the aquatic environment. As an example, under
oxidizing conditions, such as in the upper water column, heavy
metals will coprecipitate with sedimenting materials whereas in a
reducing environment, such as anaerobic bottom sediments, the
metals may be released as a result of dissolution of the iron and
manganese oxyhydroxides. In general, lower redox potentials will
favour the soluble forms of iron and manganese (Fe^{++} and Mn^{++}).

It must be pointed out that a low or negative Eh potential only
suggests a reducing potential in a medium. The actual reduction
will depend on the presence of reducing agents in the medium.

Much of the chemical reduction in bottom sediments will normally
occur in the area bordering the sediment-water interface where
organic matter containing many reducing materials accumulates. As
sediment becomes buried by new material, it is likely that further
reactions will occur only slowly in the buried material.

pH is a measure of the hydrogen ion (H^+) content of a solution.
The pH scale ranges from 0 to 14 where 7.0 is neutral pH and values
less than seven indicate acidic conditions (the lower the value the
stronger the acid) while values greater than seven indicate
alkaline conditions. pH is a very important factor in the
dissolution of minerals and ion exchange reactions. At low pH
values the H^+ in the medium will compete effectively with metal
cations for adsorption sites on particulates thus reducing the
capacity of the particulates to 'scavenge' metals from solution.
pH also controls the strength of bonds in the formation of
organic-metal complexes.

Eh and pH are closely interrelated and a change in one usually
results in a change in the other. Although they are not the only
factors controlling the fate of metals in the aquatic environment,
they regulate a variety of the other processes occurring within the
sediment-metal environment. In order to gain a good understanding
of the influence of Eh and pH on the behaviour of specific metals,
an Eh - pH diagram is usually constructed and a variety of chemical

information is summarized in the diagram. Examples of these can be found in the work of Krauskopf (1979).

2.1.6   Metal-Organic Carbon Relationships

Organic carbon, normally measured as total organic carbon (% TOC) provides an indication of the organic matter content of sediment. Organic matter from natural sources is derived mainly from animal and plant remains which are broken down by microorganisms. The most prevalent type of end products are compounds referred to as humic and fulvic acids. A variety of synthetic organic materials are also introduced into the aquatic environment via municipal and industrial discharges.

Organic carbon is very important in the formation of metal- organic complexes which remove metals from solution. In many instances a very strong positive correlation exists between % TOC and metal concentrations in sediments implying close metal-organic matter relationships. In the presence of high concentrations of minerals such as clay, no correlation or a negative correlation between metals and % TOC may exist. The most plausible explanation for this is that in the presence of high mineral content, dissolved organic matter is preferentially adsorbed onto the minerals effectively diminishing the metal-organic association (Jackson et al., 1978).

2.1.7   Sources and Properties of Toxic Heavy Metals

Arsenic: Arsenic is considered a metalloid (or semi-metal) which
           is defined as an element having both metallic and
           non-metallic properties. The major anthropogenic sources
           of arsenic include pesticides, coal and petroleum, mining
           operations and detergents. The major natural source is
           weathering.

Much of the arsenic introduced to the aquatic environment becomes bound up in the sediment, although it is quite mobile and can also be found in biota and water (Callahan, et al., 1979). The fate of arsenic is heavily dependent on the Eh and pH of the environment. It has been suggested that co-precipitation with, and adsorption to the hydrous oxides of iron and manganese are the principal mechanisms of removal of dissolved arsenic from the water column (Callahan et al., 1979). Arsenic has a biological.half-life of about seven days and can be biologically methylated.

Arsenic is quite toxic to plants and animals and therefore will not bioaccumulate in significant quantities. Bioaccumulation is usually greater at the lower trophic levels with much of the concentration in the lipid content of the organisms compared with other tissues. Fish can accumulate low levels of arsenic from their food and the water column.

Cadmium: Cadmium is rare in nature, occurring mainly in zinc bearing ores. The main sources of cadmium include zinc-bearing ores and metal refining industries. It is used in such processes as electroplating, pigment production and manufacture of batteries.

It is quite mobile in the aquatic environment where it is transported in the ionic states and readily forms complexes with organic matter. Much of the cadmium transported to sediments is through sorption to particulates especially at higher (alkaline) pH levels. The remobilization of cadmium from sediments depends mainly on the stability of its metal-organic complexes. In unpolluted and acidic waters, cadmium will exist mainly in the ionic forms which are readily accumulated by aquatic organisms.

It is highly toxic to plants and animals and there is no evidence of methylation (Callahan et al., 1979). Cadmium may be taken up by aquatic invertebrates from water, sediment and food but uptake is much lower in comparison to other metals. In fish, cadmium may accumulate in organ tissues such as the liver and gut and in the skin and gills (Moore and Ramamoorthy, 1984).

Chromium: Chromium occurs naturally as chromite ore. It is used in the preparation of corrosion resistant metal alloys, refractory bricks for high temperature uses, dyes, and in leather tanning and electroplating industries. Chromium is a biologically essential nutrient.

The chief mechanism of transport to sediment is through adsorption to organic matter and iron and manganese oxides (Moore and Ramamoorthy, 1984).

Chromium can be accumulated in aquatic organisms to levels higher than ambient water but normally lower than sediments. Although very little is known about the biotransformation of chromium, it has been demonstrated that it can be transferred through the food chain to aquatic organisms (Callahan et al., 1979). Toxicity of chromium to aquatic organisms is generally low compared with the toxicity of several other metals such as mercury, cadmium, copper, lead, nickel and zinc (Moore and Ramamoorthy, 1984).

Copper: Copper is widely distributed in nature occurring mainly as copper sulphide mineral. It is a biologically essential trace element. Copper is used mainly in electrical wires, pipe for plumbing and in biocides. In the aquatic environment, copper forms complexes with organic matter, clays and iron and manganese hydrous oxides.

The fate of copper is highly Eh and pH dependent. It has
been found that levels of copper are higher in the water
column in fall and winter and lower in spring and summer.
This has been attributed to higher bioaccumulation during
the growing season (Callahan et al., 1979).

Copper is quite toxic to aquatic organisms in the soluble
(Cu^{2+}) form. It appears to bioaccumulate in organisms
but there is no evidence of food chain biomagnification
(Callahan et al., 1979).

Lead: Lead occurs naturally in the elemental form and as a
          constituent of many minerals. Lead is used in the
          manufacture of acid storage batteries, ammunition,
          solders, leaded gasoline (tetraethyl lead) and paint
          pigments (Moore and Ramamoorthy, 1984).

          Soluble lead readily forms complexes with organic matter,
          inorganic solids and manganese oxides. Lead is quite
          mobile in acidic waters and can be remobilized from
          sediments through biomethylation.

          Lead has been found to be toxic to fish and invertebrates
          and inorganic lead can be microbially methylated to
          tetramethyl lead which is more toxic and can be rapidly
          bioaccumulated. Although lead can bioaccumulate in
          certain aquatic organisms, there is no evidence of food
          chain biomagnification (Moore and Ramamoorthy, 1984).

Mercury: Mercury occurs naturally in low concentrations in many
          types of rock and can enter the aquatic environment
          through weathering of rock. Mercury was widely used in
          pesticides, paints, pharmaceuticals, manufacture of
          chlorine, medical and dental equipment and batteries
          (Moore and Ramamoorthy, 1984). Major industrial sources
          in Ontario e.g. chloralkali plants were virtually
          eliminated in the early 1970's.

In the aquatic environment, mercury readily adsorbs to inorganic and especially organic particulates. Desorption from sediments is slow and is regulated mainly by Eh and pH (Callahan et al., 1979). Mercury can be remobilized from sediments through biomethylation and become readily available to aquatic life. The organic (methylated) forms of mercury are very toxic and can also bioaccumulate to levels affecting wildlife and humans.

Nickel: Nickel occurs naturally in the earth's crust. Nickel is used in electroplating, battery manufacture, photoengraving and in the manufacture of metal alloys (Moore and Ramamoorthy, 1984). It is one of the most mobile of the heavy metals, sorbs to organic material and coprecipitates with iron and manganese oxides, especially at pH's over 9. At lower pH's, it exists mainly in the soluble forms. In reducing environments, insoluble nickel sulphide precipitates can be formed.

Nickel is generally less toxic than most of the metals (Moore and Ramamoorthy, 1984). Nickel bioaccumulates in very low concentrations (Callahan et al., 1979).

Zinc: Elemental zinc occurs naturally in the earth's crust. Zinc is an essential nutrient. Zinc is used mainly in metallurgical industries for the preparation of alloys.

In the aquatic environment, zinc will adsorb to organic matter, iron and manganese oxides and clay minerals.

Zinc can be bioaccumulated in organisms. There is no evidence that it can be biomethylated and toxicity to aquatic organisms is relatively low compared with other heavy metals such as mercury, copper and cadmium (Callahan et al., 1979).

2.1.8 Assessing the Availability of Heavy Metals from Sediment

Traditionally, sediment assessment is based on measurement of the total concentration of contaminants (bulk chemistry). However, bulk chemistry information does not provide a clear indication of the availability of heavy metals from sediment to the water column or the biota that feed on the sediments.

The availability of heavy metals can be estimated if the quantities of metals in the various geochemical fractions of sediment are known. Various step-wise extraction schemes (selective extraction procedures) have been developed to remove metals from specific geochemical phases. The selective extraction schemes advanced to date are operationally defined by the chemical extractants used. This implies that absolute amounts of metals associated with a particular geochemical fraction may not be released in a given step. However, the schemes do provide good estimates.

The scheme outlined in table 2.1 has been developed for the In-Place Pollutants Program and is based on information published in the literature (Forstner and Wittman, 1981; Jackson et al., 1978; Tessier et al., 1979; Brannon et al., 1976; Gupta and Chen, 1975).

The first step identifies the soluble metals present in the interstitial (pore) water (IW). This fraction is considered to be readily available to the aquatic biota (Forstner and Wittman, 1981).

The second step identifies the weakly adsorbed fraction of metals. This fraction is associated with sediments mainly through physical adsorption. The metals (+ve charge) attach (non-specifically) to negatively charged surfaces of·clays and organic particulates. The metals in this phase (F1) are in equilibruium with the water soluble phase (IW).

TABLE 2.1 SELECTIVE EXTRACTION SCHEME

STEP	PHASE	EXTRACTANTS
1	Interstitial water (IW)	Centrifuge at 15,000 rpm/10 min.
2	Weakly adsorbed and cation exchangeable (F1)	1M NH_4OAC (ammonium acetate)
3	Specifically adsorbed and easily reducible (F2)	0.1M $NH_2OH.HCl/HNO_3$ (Hydroxylamine hydrochloride,(pH 2)
4	Organic Complex (F3)	30% H_2O_2 + HNO_3 + NH_4OAC (pH 2) (Acidified hydrogen peroxide, followed by NH_4OAC extraction) at 95°C.
5	Coprecipitates (F4) (reducible Fe/Mn hydroxides)	1.0M $NH_2OH.HCl/HOAC$ (25% V.V) at 95°C
6	Residual (F5)	$HNO_3:HClO_4$ (2:1, V:V) at 150°C.

Step three examines the specifically adsorbed (chemical adsorption) and easily reducible fraction (F2). The specifically adsorbed metals differ from those in phase F1 in that the association is stronger than mere electrostatic adsorption. The metals form weak bonds with the solids. The chemical extractants used in this step selectively dissolve the manganese oxides while having little effect on the iron oxides. Release in the natural environment can be triggered under reducing (anaerobic) conditions.

The fourth step releases the metals associated with organic complexes and sulphide compounds (F3). In the natural environment metals from sulphides can be released under oxidizing conditions (change in redox potential). Organic matter can be degraded under oxidizing conditions, releasing metals (Jackson et al., 1978).

The fifth step identifies the metals sorbed to iron and manganese oxides (F4). These oxides can exist as nodules, concretions or coatings on particulates. They are good scavengers of metals but are unstable under anaerobic conditions (low Eh) (Jackson et al., 1978).

The sixth step identifies the residual phase (F5). The metals in this phase are 'inertly' bound within the crystal lattice of minerals and are normally unavailable in the sedimentary environment.

2.2 SOURCES AND PROPERTIES OF PCB's AND ORGANOCHLORINE PESTICIDES IN THE AQUATIC ENVIRONMENT

The organochlorine compounds (OC) selected for this study are the group routinely analyzed in a PCB-OC Scan. These include polychlorinated biphenyls (PCB's); the cyclodiene pesticides-aldrin, dieldrin, endrin, endosulfan, chlordane, heptachlor and mirex; hexachlorobenzene; DDT and its metabolites DDD and DDE and the methoxy analogue of DDT, methoxychlor.

Unlike the heavy metals which can be derived from natural sources, the organochlorine compounds listed above are synthetically derived and enter the aquatic environment through industrial, agricultural and domestic uses and in some cases, deposition from the atmosphere. Many of these compounds are extremely persistent (long-lived) and have a high affinity for particulate matter. They are often transported to lake and river sediment where some, notably DDT, PCB, mirex, endosulfan and dieldrin, persist for many years.

In addition to sorption onto particulate matter, there are a variety of other processes governing the fate of organochlorine compounds in the aquatic environment. Some compounds can be volatilized from surface waters to the atmosphere while the process of photolysis (degradation by sunlight) can degrade certain compounds. Because of the lipophilic (fat soluble) nature of many organochlorines and their low solubility in water, many of them will be preferentially taken up in the lipid pool (fatty tissue) of aquatic organisms. Organisms are capable of breaking down (metabolize) certain compounds but if the rate of degradation is less than the rate at which the organism is accumulating the compound, it may bioaccumulate in the organisms. The metabolic breakdown of biodegradable compounds often results in products (metabolites) that exhibit different physical and chemical properties from the parent compound.

Compounds that bioaccumulate can be transferred through the food chain
with organisms in each of the higher trophic levels showing higher
concentrations - a process referred to as biomagnification. Notable
examples of compounds that are biomagnified are DDT and PCB's. These
substances can accumulate in fish to levels that have necessitated the
publication of Fish Consumption Advisories (MOE and MNR, 1986) and as
well, the establishment of criteria to protect fish eating birds (IJC,
1977).

Many of the organochlorine compounds are not acutely toxic to aquatic
organisms but may result in subtle physiological changes that remain
unnoticed until they become chronic. The subtle effects may result in
genetic or reproductive changes that can substantially alter the numbers
or types of organisms inhabiting a particular environment.

2.2.1 Environmental Properties of PCB's and Organochlorine Pesticides

Aldrin, Dieldrin and Endrin

Aldrin, ($C_{12}H_8Cl_6$) is an organochlorine insecticide that when
applied to the environment, rapidly volatilizes or is readily
converted to its epoxide, dieldrin ($C_{12}H_8Cl_6O$). Because aldrin is
quickly converted to dieldrin, aldrin is not readily bioaccumulated
by aquatic biota. Dieldrin is very persistent in the environment.
It bioaccumulates in animal tissues from which it is eliminated
very slowly. It is a very effective insecticide against termites
and residues resulting from soil application of aldrin are
insecticidal for several years. Aldrin and dieldrin have not been
used in substantial amounts in Ontario for several years. Dieldrin
can be oxidized to its stereo-isomer (endo-endo isomer) endrin.
Endrin ($C_{12}H_8Cl_6O$), was an insecticide applied to the soil but has
not been used since the late 1960's. It is environmentally very
persistent, may be bioaccumulated by aquatic biota and is very
toxic to fish (McEwen and Stephenson, 1979) and mammals (Worthing,
1983).

Endosulfan (I and II) and Endosulfan Sulphate

Endosulfan ($C_9H_6Cl_6O_3S$) is currently used as an insecticide for vegetable production in Ontario.   It consists of a mixture of two isomers - alpha endosulfan or endosulfan I (making up about 70% of technical endosulfan) and beta endosulfan or endosulfan II (comprising about 30% of technical endosulfan). Endosulfan is only slightly soluble in water, very soluble in organic solvents, but does not bioaccumulate in significant amounts. The beta-isomer can persist for over a year. Both isomers can be oxidized to endosulfan sulphate, ($C_9H_6Cl_6O_4S$) the major metabolite which is very toxic to fish (McEwen and Stephenson, 1979).

Heptachlor ($C_{10}H_5Cl_7$) is an insecticide also known as heptachlorodicyclo-pentadiene but has not been used since the mid 1960's. In the aquatic environment it will undergo rapid hydrolysis. Portions that are not hydrolyzed will bioaccumulate (Callahan et al., 1979). It is a very persistent insecticide with significant potential for biomagnification. Heptachlor may be highly toxic to aquatic biota (Pers. Comm. N. Bazinet).

Heptachlor epoxide ($C_{10}H_5Cl_7O$) is a metabolite of heptachlor. It is highly persistent in the environment (being resistant to biological or chemical transformation) and very toxic to aquatic biota (Pers. Comm. N. Bazinet).

Mirex ($C_{10}Cl_{12}$) is an insecticide that was used in the Southern U.S.A. for the control of fire ants. Mirex was manufactured until the mid-1970's on the U.S. side of the Niagara River. Significant impacts in Ontario are limited primarily to Lake Ontario from U.S.A. sources. It was also used as a flame retardant agent under the name of dechlorane. Mirex is extremely persistent, insoluble in water and readily bioaccumulates in organisms since it is lipophilic.

Chlordane ($C_{10}H_6Cl_8$) an insecticide applied to soil, is made up of primarily alpha and gamma chlordane. The use of chlordane has been

discontinued in Ontario except for termite and carpenter ant control. It is fairly insoluble in water and soluble in most organic solvents. There is no evidence of bioaccumulation. It is very persistent in soil (McEwen and Stephenson, 1979), (1/2 life ≈ 3 years) and it is highly toxic to aquatic biota (Pers. Comm. N. Bazinet).

Hexachlorobenzene or Perchlorobenzene (C_6Cl_6) is a member of a group of compounds referred to as the chlorinated benzenes.

Hexachlorobenzene (HCB) is generated as a byproduct in the productions of such compounds as perchloroethylene, carbon tetrachloride and trichloroethylene. It can also occur as a 'contaminant' in these products.

In 1945, HCB was introduced as a fungicide for cereal and seed treatment in the U.S. and although it is not a registered pesticide in Canada it is widely used in the control of wheat bunt.

HCB is very stable chemically and very resistant to biotic and abiotic degradation. It is very lipophilic and bioaccumulates rapidly. It is excreted very slowly from aquatic biota (MOE, 1984).

DDT and Related Compounds. DDT was a widely used insecticide in Ontario between 1950 and 1970. It is one of the most persistent insecticides, virtually insoluble in water, lipophilic and soluble in most organic solvents. It can bioaccumulate in fats of organisms. DDT can be metabolized to DDD and DDE. DDE is the form most commonly found in sediments and biological life. It can persist in the environment for decades. DDD (one less Cl atom than DDT) is also insecticidal. DDT undergoes significant biomagnification and is highly toxic to aquatic biota (Pers. Comm. N. Bazinet).

Methoxychlor is the methoxy analogue of DDT. It does not persist in the environment. Some organisms can metabolize methoxychlor but

those organisms that cannot may bioaccumulate small quantities of
the compound. It is currently used as an insecticide in
agricultural and domestic sectors in Ontario. Fish have been found
to concentrate methoxychlor but the residues are lost once the
source is eliminated (McEwen and Stephenson, 1979). Methoxychlor
can be highly toxic to aquatic biota (Pers. Comm. N. Bazinet).

Polychlorinated Biphenyls (PCB's)

PCB's are a group of compounds consisting of a biphenyl molecule
with differing numbers and arrangement of chlorine atoms. The
physical and chemical properties of PCB's are determined mainly by
the positions and numbers of chlorine atoms on the biphenyl
molecule. As a result, individual PCB's vary in physical and
chemical properties. In general, PCB's with five or more chlorine
atoms are very resistant to natural degradation processes while
molecules with less than five chlorine atoms can be biodegraded
(Callahan et al., 1979).

PCB's are known by a variety of trade names e.g., Aroclor (USA),
Phenochlor (France), Kanechlor (Japan), etc. The Aroclor series
manufactured in the USA are identified by a four digit code e.g.,
Aroclor 1254. The first two digits (12) indicate that the
preparation is a PCB mixture, while the last two digits (54)
indicate the mixture has 54% chlorine.

PCB's are very inert to chemicals such as acids and alkalies, very
resistant to heat and have a high dielectric constant. These
properties make them ideal for uses in dielectric fluids, heat
transfer agents, plasticizers, sealants and adhesives.

PCB's are virtually insoluble in water but are soluble in
hydrocarbon compounds (solvents and fats). In the aquatic
environment they will selectively partition to the lipid pool of
organisms where they can bioaccumulate and can be transferred up
the food chain. PCB's also strongly adsorb to sediments rich in
organic carbon (highly organic sediments). However they have a

greater affinity for oils than for sediments (Callahan et al., 1979).

2.2.2.   Assessing the Availability of PCB's and Organochlorine Pesticides from Sediment

Selective chemical extraction schemes analogous to those used in assessing the availability of metals from sediment have not been developed for PCB's and pesticides. As a result, chemical analytical techniques only provide information on the total concentrations of these compounds in sediment.

Of the total amounts of these compounds in sediment however, only a fraction may be bioavailable and release to the watercolumn may be very slow depending on the constituents of the sediment matrix. Studies have shown that pesticides such as DDT are strongly associated with the solvent extractable material (oils and greases) in sediment (Hartung and Klinger, 1970). Other studies have shown that although benthic organisms can accumulate PCB's directly from sediment, the presence of solvent extractable materials greatly inhibits this process (Meier and Rediske, 1984).

PCB's and pesticides also have strong affinities for fine particulate matter such as organic material. In the presence of organic matter, especially the refractory organics such as chitins and lignins which are very resistant to degradation, the contaminants may be rendered largely unavailable.

In general, sediments that are contaminated with PCB's and pesticides but have significant levels of organic matter and oil and grease may not present any significant short-term problems in relation to contaminant biouptake or release to the water column. There would, however, be long-term concerns related to the gradual breakdown of the oils and greases and organic matter through microbial degradation. Studies have shown that the less persistent pesticides are very readily degraded in anaerobic sediments (Muir and Yarechewski, 1984) which should result in a rapid decline in

their concentrations in anaerobic sediment once active sources have been eliminated.

With regards to the more persistent compounds such as PCB's, microbial degradation of organic matter and oils and greases in sediment may result in their gradual release to the surrounding water, in which case they would be more readily available to biota. It has been demonstrated that uptake from solution is a very rapid and effecient process compared to uptake from sediment (Fowler et al., 1978). Contaminant availability may also be increased as a result of the resuspension of contaminated sediments. Fish exposed to contaminated suspended sediments have been shown to accumulate contaminants from them (Seelye et al., 1982).

Sediment type can also influence the availability of organic contaminants. It was found that shrimp exposed to PCB contaminated mud and sand showed greater concentration factors in the sandy substrate (McLeese et al., 1980).

The availability of PCB's and pesticides from sediment would therefore be very site-specific and would be influenced by the type of sediment and the presence of oils and greases and organic matter.

2.3 BENTHIC ORGANISMS - CONTAMINANT INTERACTIONS

The most obvious adverse effects of pollutants on aquatic organisms are often the dramatic events associated with sudden mortality such as fish kills. Other effects are more subtle such as sublethal effects on reproduction, growth, etc. which may result in the diminution or elimination of sensitive organisms. Benthic organisms which inhabit aquatic bottom sediments often encounter high levels of contaminants since sediments are a repository of many contaminants introduced into the aquatic environment. Many of these organisms are restricted in their mobility and must live in and feed on the contaminated material.

In areas of high sediment contamination, some organisms cannot survive while others have a 'tolerance' for certain levels of pollution. The organisms take up contaminants from the surrounding water and through ingestion of sediments which can be altered by bacteria and digestive enzymes in the gut.

The biological focus of this investigation is on benthic macroinverte-brates that spend a considerable portion of their life cycles in bottom sediments and that are also important in the diet of fish. The oligo-chaetes and chironomids have been selected for the In-Place Pollutants Program because of their predominance and wide distribution in the Great Lakes (Nalepa and Thomas, 1976; Freitag et al., 1976).

The oligochaetes spend their entire life cycle in sediments and the chironomids spend the larval portion of their life cycle in bottom sediments.

Both of these groups of organisms are fed upon by certain species of fish (Sly, 1984) and in some instances may form a significant portion of the fish diet. In a study carried out in Lake Superior, it was noted that chironomid pupae constituted almost 75% of the food of young-of-the-year lake trout (Swedberg and Peck, 1984). This is especially significant in light of studies (Eadie et al., 1982; Meier and Rediske, 1984) which show that benthic organisms can take up contaminants directly from sediments and evidence (Bryan, 1979) that suggest the main source of organochlorines such as DDT and PCB's to fish is through dietary sources.

The fate of contaminants in an organism depends on a variety of physiological and biochemical factors in the organism and the chemical form of the pollutants. The levels to which organisms accumulate a certain pollutant depend on their ability to store or excrete the pollutant (Bryan, 1979). Three major types of relations between the levels of contaminants in the environment and organisms have been suggested (Bryan, 1979). These are: increases in body burden are proportional to levels being taken in from the environment; the rate of storage exceeds the rate of excretion (body burden increases with age); and levels of contaminants in the organism are independent of those in the environment (i.e. the organism excretes or metabolizes most of the contaminants encountered).

One of the major concerns with the transfer of contaminants from benthic organisms through the food chain is the progressively higher concentrations that can be retained at the higher trophic levels - a process commonly referred to as biomagnification. This has only been clearly demonstrated for the organochlorines DDT and PCB's and the metals zinc, mercury and arsenic (Biddinger and Gloss, 1984). The In-Place Pollutants Program has initiated studies that sample bottom-feeding fish (sculpins) in order to address the issue of biomagnification.

An understanding of the fate and distribution of contaminants in benthic organisms requires a good knowledge of the physical and chemical factors regulating contaminant availability in the environment, the physico-chemical factors influencing contaminant bioaccumulation in organisms, the influence of organism size, age and sex to contaminant uptake and the significance of food and water as routes of uptake and habitat. Much progress has been made to advance our knowledge in these areas (Biddinger and Gloss, 1984; Bryan, 1975). However, there are still a number of gaps to be bridged in order to obtain a comprehensive understanding of the fate and significance of various levels of environmental contaminants.

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